Theoretical investigation of TbNi$_{5-x}$Cu$_x$ optical properties

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In this paper we present theoretical investigation of optical conductivity for intermetallic TbNi$_{5-x}$Cu$_x$ series. In the frame of LSDA+U calculations electronic structure for $x = 0, 1, 2$ and on top of that optical conductivities were calculated. Disorder effects of Ni for Cu substitution on a level of LSDA+U densities of states (DOS) were taken into account via averaging over all possible Cu ion positions for given doping level x. Gradual suppression and loosing of structure of optical conductivity at 2 eV together with simultaneous intensity growth at 4 eV correspond to increase of Cu and decrease of Ni content. As reported before [Knyazev *et al.*, Optics and Spectroscopy **104**, 360 (2008)] plasma frequency has non monotonic doping behavior with maximum at $x = 1$. This behavior is explained as competition between lowering of total density of states on the Fermi level $N(E_F)$ and growing of number of carriers. Our theoretical results agree well with variety of recent experiments.

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I. INTRODUCTION

Intermetallic compounds of RNi$_5$-type have been attracting considerable interest initiated by their remarkable physicochemical properties and potential applications as materials with high hydrogen storage capacity[1]. Their physical properties, which are characterized by a large variety of magnetic structures and electronic peculiarities, have been actively investigated, both theoretically and experimentally. Substitution of one rare-earth metal R with another one modifies significantly these characteristics because of crystal field effects and changes of exchange interaction value between the conduction and 4f-localized electrons.

On the the other hand substitution of Ni for some other transition metal also leads to interesting physical phenomena. For example, series of isostructural RNi$_{5-x}$Cu$_x$ alloys was found experimentally to have non monotonic concentration dependence of the magnetic susceptibility, Curie temperature T$_C$, electronic specific heat and resistivity[3–7]. A number of studies indicate a direct correlation between this anomalous behavior of the parameters and band structure evolution with copper content increase[4,5,8]. To explain these experimental data one needs more detailed investigation of electronic structure of the RNi$_{5-x}$Cu$_x$ series for different x.

There are several experimental and theoretical works on the RNiCu compounds. X-ray photoemission study of LaNi$_{5-x}$Cu$_x$ solid solution shows presence of Cu-3d band, which is located almost 2 eV below the 3d band of Ni and is weakly hybridized with the latter one[8]. The calculation of Ref. 5 predicts the existence of a wide ($\sim$ 1,5 eV) peak in the electron density of states of the YNi$_{5-x}$Cu$_x$ alloys at energies 2.5-4 eV below Fermi level E$_F$, which is related to the 3d electrons of Cu. The evolution of frequency dependencies of the optical conductivity of the TbNi$_{5-x}$Cu$_x$ compounds upon substitution of Ni for Cu atoms investigated in Ref. 10. There it was observed that a new structure arises in the optical spectra (a broad absorption maximum peaking at 4 eV) while the Cu content increases. Detailed investigation of crystal structure and thermodynamic properties from both experimental and band structure calculation sides is done in Ref. 9 (except

for the optical properties).

Within this study we continue investigation of the electronic structure of TbNi$_{5-x}$Cu$_x$ isostructural alloy series with $x = 0, 1, 2$ by carrying out self-consistent *ab initio* LSDA+U calculations. Disorder effects are taken into account in a combinatorial way with respect to possible number of Cu positions for given doping. Corresponding averaged over the Cu positions spin resolved densities of states are calculated. Following it interband contribution to the theoretical optical conductivity is determined. Drude (intraband) contribution is taken as a Lorentzian with experimentally determined parameters. Comparison of our theoretical results with recent optical experiment is presented.

II. CALCULATION OF THE ELECTRONIC STRUCTURE

The TbNi$_5$ compound crystallizes into a hexagonal structure of the CaCu$_5$ type with a space group P6/mmm and lattice parameters for x=0 — $a=b=$4.8988 Å and $c=$3.96 Å (see Fig. 1), x=1 — $a=b=$4.9126 Å and $c=$3.9901 Å and x=3 — $a=b=$4.9351 Å and $c=$4.0113 Å.[9] The nickel has two inequivalent crystallographic positions Ni1(2c) (1/3,2/3,0) and Ni2(3g) (1/2,0,1/2), Tb has a position 1(a) (0,0,0). In Fig. 1 Ni1 ions are represented by violet circles and located in the same "layer" as Tb ions (green circles, Fig. 1). The Ni2 ions (red circles, Fig. 1) also form a "layer".

A calculations of the electronic structure of TbNi$_{5-x}$Cu$_x$ ($x = 0, 1, 2$) were performed within the linear muffin-tin orbitals (LMTO) method[11]. The program package TB-LMTO-ASA (tight-binding LMTO together with atomic spheres approximation) v. 47 was employed[12]. The subdivision of the first Brillouen zone in the reciprocal space is (10 10 10) with 132 irreducible **k**-points. The atomic sphere radius for Tb was obtained to be about 3.47 a.u., for nickel and copper ions about 2.63 a.u. The orbital basis consists of 6s, 5d and 4f muffin-tin orbitals for Tb, and 4s, 4p and 3d for Cu and Ni. LSDA+U calculations on top of that were done as proposed in Ref. 14 with Coulomb interaction parameters for Tb(4f) states $U = 5.4$ eV and $J = 0.7$ eV.[15] Also recently we showed that
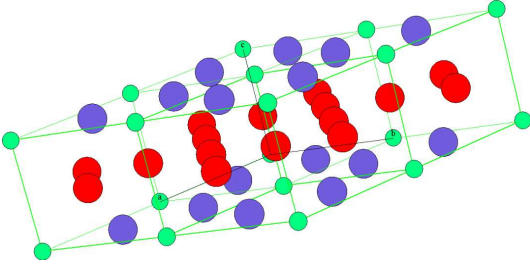
FIG. 1: (Color online) TbNi$_5$ crystal structure. Tb ions – green circles, Ni1,Ni2 – violet and red circles correspondingly.

Coulomb interaction for Fe ions in intermetallides is almost completely accounted within LSDA by itself.[13]

To introduce Cu into the TbNi$_5$ system one or two Ni ions were substituted with Cu. To mimic disordered alloy we perform calculations for different possible positions of copper ions for chosen doping level x. Assuming that each possible Cu position has the same weight we then average obtained partial densities of Ni and Cu-3d states with following ratios for corresponding Ni Wickhoff positions: for $x = 1$ i.e. one copper ion 2(2c):3(3g) and $x = 2$, two Cu ions, 1(2c):3(3g):6(2c+3g).

In our LSDA+U calculations collinear ferromagnetic order of the local magnetic moments on all lattice sites was chosen. Moreover the terbium and nickel sublattices are taken to be ferromagnetic with respect to each other. In this compound main magnetic moment is localized on terbium ions while nickel ions have a small magnetization because of almost completely occupied Ni-3d shell in accordance with Ref. 2. For parent TbNi$_5$ system local magnetic moments in units of Bohr magneton are following: on Tb(5.8), Ni1(0.27) and Ni2(0.28). Total magnetic moment of TbNi$_5$ is 7.21 Bohr magneton. With Ni for Cu substitution in TbNi$_5$ depending on Cu position total magnetic moment goes down about 10-15%. These results agree well with experimental data of Ref. 9. Local magnetic moments on nickel ions become two to three times smaller. Local magnetic moment on terbium insignificantly grows, while copper stays practically non magnetic.

The Fig. 2 shows the total (upper panel) and partial Ni(3d) (middle panel) and Cu(3d) (lower panel) DOSes for up (↑) and down (↓) projections of local spin moments for the ferromagnetic TbNi$_{5-x}$Cu$_x$ (x=0,1,2) compounds. Structure of these DOS for different x is rather similar to each other and agrees with Ref. 9 for stoichiometric TbNi$_5$. It is seen that the main spectral weight is located below the Fermi level. The 3d states of Ni1 and Ni2 form the wide bands extending from 4.0 to 0.5 eV. The 3d states of Cu1 and Cu2 bands for the compounds with x=1,2 are located in the energy range -4~-6 eV below E$_F$. Their width is considerably smaller with respect to Ni-3d states. The 4f-states of Tb ion for majority spin are located below -6 eV and for minority at about 1.5 eV.

III. OPTICAL CONDUCTIVITY RESULTS AND DISCUSSION

Calculated LSDA+U band structures presented in the previous section are used to interpret experimental optical data[10] for the systems under consideration. In order to calculate theoretical interband optical conductivity σ_{theor} we applied a rather simplified technique[16] using approximation, that the direct and indirect (involving phonons) interband transitions are equally probable. Namely we computed σ_{theor} like the integral function based on the convolution of the density of states located both below and above the E_F. The electronic transitions of the d→f type are not observed in the calculation due to their low probability. This technique was already successively applied by us to intermetallic R$_2$Fe$_{17}$ compounds[15].

From total LSDA+U DOS presented on upper panel of Fig. 2 one can observe decrease of total DOS on the Fermi level $N(E_F)$ with Cu doping. It happens because for x=0 $N(E_F)$ consists mostly of Ni-3d states. With doping number of Ni ions goes down while newly introduced Cu ions do not contribute to the $N(E_F)$ (see lower panel of Fig. 2).

Figure 3 displays corresponding theoretical optical conductivity $\sigma_{theor}(\omega)$ (solid lines) together with experimental fre-qu

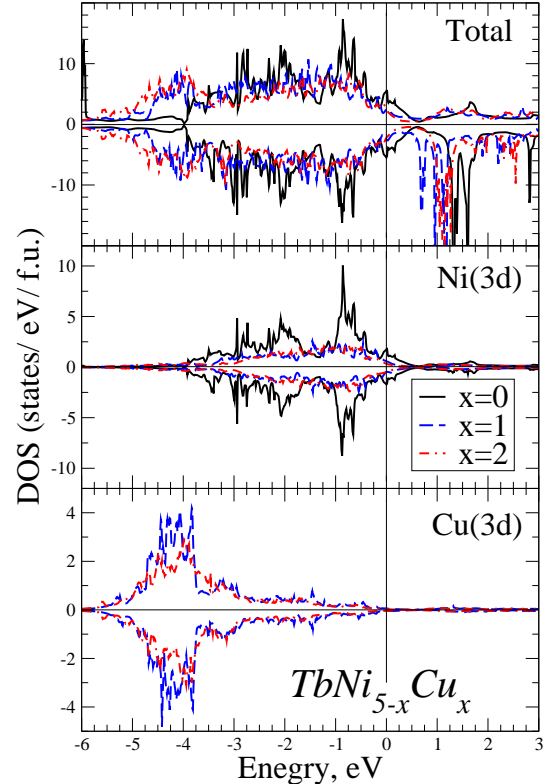FIG. 2: (Color online) LSDA+U calculated DOS for TbNi$_{5-x}$Cu$_x$. Upper panel – total DOS; middle panel – Ni-3d states; lower panel – Cu-3d states. In all graphs solid black line represents TbNi$_5$; dashed blue lines – averaged DOS for TbNi$_4$Cu$_1$; dash-dot red line – averaged DOS for TbNi$_3$Cu$_2$. Fermi level corresponds to zero.
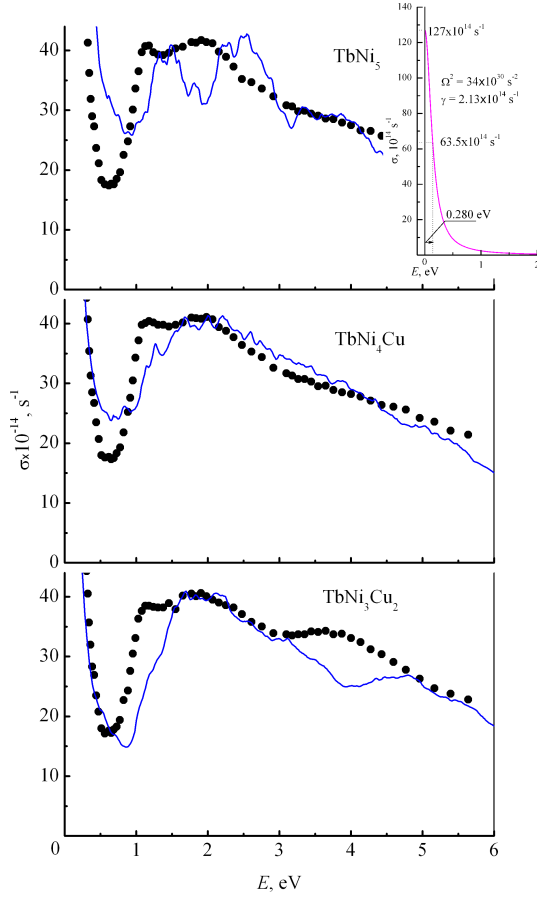
FIG. 3: (Color online) Comparison of experimental optical conductivity (dots) and theoretical one (solid line in arbitrary units) for different doping levels x=0,1,2 (from top to bottom) for TbNi$_{5-x}$Cu$_x$. In the inset of upper panel Drude peak and corresponding experimental parameters of the Lorentzian are shown.

for TbNi$_{5-x}$Cu$_x$ ($x = 0, 1, 2$ from top to bottom). In the energy region below ~ 0.5 eV the behavior of $\sigma(\omega)$ for all compositions sharp Drude peak is determined experimentally. Corresponding height and width of Drude peak (127×10^{14} s^{-1} and 0.280 eV for $x = 0$, 156×10^{14} s^{-1} and 0.278 eV for $x = 1$, 130×10^{14} s^{-1} and 0.288 eV for $x = 2$) were extracted from these curves and then used to draw theoretical one (see inset of Fig. 3). As follows from above mentioned static conductivity (Drude peak height) it goes down with doping. It agrees with lowering of $N(E_F)$ in our LSDA+U calculations since conductivity is proportional to $N(E_F)$. In its turn plasma frequency is also proportional to $N(E_F)$ and thus should decrease with Cu doping. On the other hand substitution of Ni for Cu adds one electron to the system and increases number of carriers. Plasma frequency squared is proportional to the number of carriers (in the simplest Drude-like picture) and then should grow with Cu doping. These two competing tendencies lead to the non monotonic doping behavior of plasma frequency recently observed experimentally in Ref. 10.

At energies above 0.7 eV the shape of $\sigma(\omega)$ dispersion in-

dicates the dominant role of interband absorption. The wide absorption region is characterized by structures, which intensities and localizations depend on the compound composition. The optical conductivity of the TbNi$_5$ binary alloy (upper curve) exhibit two peaks at photon energies 1.15 and 1.9 eV respectively. In the TbNi$_4$Cu compound the $\sigma(\omega)$ spectrum is almost the same; we can only note that the minimum between these structures is less pronounced. With a further increase in the Cu content ($x = 2$) a new fairly broad absorption band arises at energies 3-4.5 eV.

Corresponding theoretical optical conductivity curves σ_{theor} shows evolution upon substitution of nickel with copper similar to experimental one. Theoretical calculations reproduce qualitatively the basic features of the experimental spectra, namely, two-peak structure at 1-2.5 eV, associated with the Ni 3d interband transitions. The depth about 1.5 eV is getting closed. High energy tail above 3 eV becomes smoother with doping increase and for $x = 2$ one can see the formation of the "Cu-states" peak at about 5 eV. Somewhat higher energy position of leading interband absorption edge (about 1 eV) might come from uncertainties in computation of U value.

IV. CONCLUSION

In this work we perform *ab initio* LSDA+U computations of electronic structure of intermetallic isostructural alloys TbNi$_{5-x}$Cu$_x$ ($x = 0, 1, 2$). Disorder effects of Ni for Cu substitution were accounted in a combinatorial way. Corresponding averaged over all possible Cu positions for given doping level x DOS are further used to compute theoretical optical conductivity. Here we is theoretically explain how experimental optical conductivity line shape changes with doping. Analyzing LSDA+U calculated DOS one can find that responsible for the structures of optical conductivities at 1-2 eV electronic states are predominantly Ni-3d states, while at ~4-5 eV there are Cu-3d states. Amount of latter ones increases upon doping giving rise to the structure at 4-5 eV in optical conductivity. One should note also good semiquantitative agreement between theoretical and experimental data. Finally in this work we give explanation of the experimentally observed maximum of plasma frequency for x=1[10] as competition of lowering of $N(E_F)$ and simultaneous growing of number of carriers with Ni for Cu substitution.

V. ACKNOWLEDGEMENTS

[1] J. J. Franse and R. J. Radvansky, Handbook of Magnetic Materials, Ed. by K. H. J. Buschow, (North-Holland, Amsterdam) 7, p. 307 (1993)

[2] K. H. J. Buschow, Rep. Progr. Phys. 40, p. 1179 (1977).

[3] A. G. Kuchin, A. S. Ermolenko, V. I. Khrabrov, N. I. Kourov, G. M. Makarova, Ye. V. Belozerov, T. P. Lapina and Yu. A. Kulikov, J. Magn. Magn. Mater. 238, p. 29-37 (2002).

[4] A. M. Gurevich, V. M. Dmitriev, A. S. Ermolenko, V. E. Eropkin, A. G. Kuchin, N. N. Prentslau and A. V. Terekhov, Fiz. Nizk. Temp. 27, p. 896-900 (2001).

[5] G. E. Grechnev, A. V. Lagosha, I. V. Svechkarev, A. G. Kuchin, Yu. A. Kulikov, P. A. Korzhavyi and O. Eriksson, Fiz. Nizk. Temp. 32, p. 1498-1506 (2006).

[6] A. G. Kuchin, A. S. Ermolenko, Yu. A. Kulikov, V. I. Khrabrov, E. V. Rosenfeld, G. M. Makarova, T. P. Lapina and Ye. V. Beloserov, J. Magn. Magn. Mater. 303, p. 119-126 (2006).

[7] A. N. Pirogov, J.-G. Park, A. S. Ermolenko, A. V. Korolev, A. G. Kuchin, S. Lee, Y. N. Choi, J. Park, M. Ranot, J. Yi, E. G. Gerasimov, Yu. A. Dorofeev, A. P. Vokhmyanin, A. A. Podlesnyak, I. P. Swainson, Phys. Rev. B 79, 174412 (2009).

[8] E. Burzo, S. G. Chiuzbian, L. Chioncel and M. Neumann, J. Phys.: Condens. Matter 12, p. 5897-5904 (2000).

[9] R. Lizárraga, A. Bergman, T. Bj orkman, H.-P. Liu, Y. Andersson, T. Gustafsson, A.G. Kuchin, A.S. Ermolenko, L. Nordstr om, O. Eriksson, Phys. Rev. B 74, 094419 (2006).

[10] Yu. V. Knyazev, Yu. I. Kuzmin, A. G. Kuchin, A. V. Lukoyanov and I. A. Nekrasov, Optics and Spectroscopy 104, p. 360-365 (2008).

[11] K. Andersen . Phys. Rev. B. 12, 3060 (1975).

[12] O. K. Andersen, O. Jepsen., Phys. Rev. Lett. 53, 2571 (1984).

[13] A.V. Lukoyanov, E.E. Kokorina, M.V. Medvedev, I.A. Nekrasov, Phys. Rev. B 80, 104409 (2009).

[14] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys.: Condens. Matter 9, 767 (1997).

[15] Yu. V. Knyazev, A. V. Lukoyanov, Yu. I. Kuzmin, A. G. Kuchin, I. A. Nekrasov, Phys. Rev. B. 73, 094410 (2006) and references therein.

[16] C. N. Berglund, W. E. Spicer , Phys. Rev. 136, A1044 (1964).